Tetrahedron. Vol. 26, pp. 5195–5200. Pergamon Press 1970. Printed in Great Britain

HIGH TEMPERATURE REACTIONS OF BENZENE

R. A. FIRESTONE and J. S. AMATO
Merck, Sharp & Dohme Research Laboratories
Division of Merck & Co., Inc., Rahway, N.J. 07065

(*Received in the USA* 16 *April* 1970; *Received in the UK for publication* 20 *July* 1970)

Abstract—High temperature reactions of benzene with olefins and acetylenes are described, and interpreted as Diels–Alder, retrodiene and related steps. The results are discussed in terms of both concerted and diradical mechanisms.

BENZENE is a reluctant diene, undoubtedly owing to its aromaticity. Nevertheless, it does undergo the Diels–Alder reaction at moderate temperatures with highly reactive acetylenic dienophiles.[1] Over 100 years ago, reactions of benzene at high temperatures with unactivated dienophiles were described[2] which we interpret as diene and retrodiene syntheses, along with other reactions. We report herein further reactions of benzene, performed at atmospheric pressure in a flow apparatus at temperatures up to 668°.

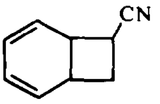
RESULTS

Benzene reacted with itself at 656–659° to produce biphenyl, with conversion of 2·5% after 24 sec. This product, *inter alia*, was observed by Berthelot.[2] From benzene and cyanoacetylene at 662–665°, essentially only biphenyl and benzonitrile were obtained, in approximately equal amounts; conversion was 1–2% in 13 sec. This constitutes, in effect, a type of aromatic substitution. With methyl propiolate at 653–660°, benzene afforded a plethora of products after 24 sec, among them methyl benzoate. That the latter was a primary product was shown by successively shortening the contact time to 12 and then 6 sec, which caused steady diminution of most of the VPC peaks other than methyl benzoate. Its poor thermal stability compared to that of benzonitrile, which can be put through the hot tube virtually unchanged, is in accord with the facts that singly-bond dissociation energies are especially low adjacent to carbonyl, but especially high adjacent to triply bonded carbon.[3]

With an ethylenic dienophile under similar conditions, one might have expected comparatively little reaction, since now the retrodiene step can produce an aromatic product only by reversion to reactants. However, acrylonitrile proved to be about as reactive as cyanoacetylene, affording, with an equimolar amount of benzene at 660–661°, *ca* 3% conversion after 30 sec. There were four principal products, formed in commensurate amounts, along with a lesser quantity of biphenyl. Stepwise reduction in contact time to 11, 4 and 2 sec reduced the percent conversion but effected no change in the VPC spectrum, showing that the various products were formed nonsequentially, were thermally stable. and did not react with one another. The products were identified as benzonitrile,* *cis*- and *trans*-cinnamonitrile, and *o*-cyanostyrene. Lowering the temperature in 50° steps at 15 sec contact time reduced the conversion to < 0·2% at 596–604°, and only traces at 546–550°. In addition, the composition of the product changed, with benzonitrile falling away fastest.

Control experiments reinforced the evidence above that the products—in particular *o*-cyanostyrene, which was of greatest interest—were not formed from each other. *trans*-Cinnamonitrile alone at 653–664° afforded some *cis* isomer but no *o*-cyanostyrene; the latter was also not formed from benzonitrile and acrylonitrile.

These results are compatible with, but do not require, the formation of all the products (save biphenyl) from a single intermediate which can undergo several further reactions whose activation requirements differ. If there is a single intermediate, it cannot be the 1,2-adduct I, a known compound,[4] because this substance at 652–660° (30 sec) produced, in addition to the expected mixture of benzene and acrylonitrile, benzonitrile in 10% yield as the only other important product.

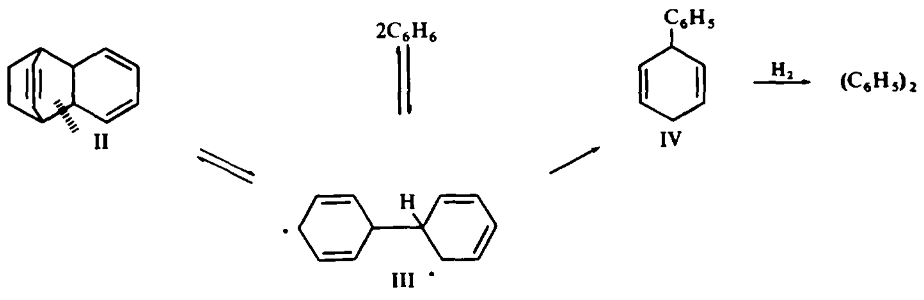


I

DISCUSSION

Although the concerted mechanism for the Diels–Alder reaction is favored by most authorities in the field,[5] the diradical mechanism[6] is still in contention. The present results will be discussed in both terms.

The normal Diels–Alder dimer of benzene, and the only symmetry-allowed thermal one,[7] is II. Its transformation, via the diradical III, to IV and then biphenyl is straightforward, with all steps well precedented.

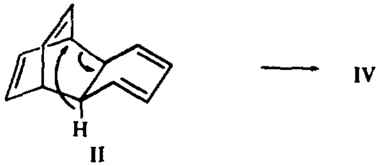


---

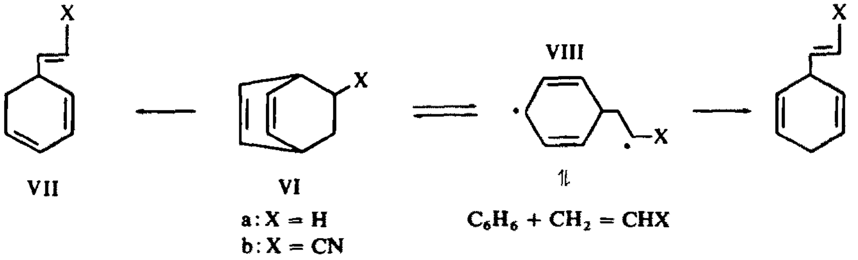
* Acrylonitrile alone survived 13 sec at 659° in >99% purity by IR and VPC analysis. However, benzonitrile was detected in minute amounts, casting some doubt on the significance of its presence in the acrylonitrile-benzene experiments. We nevertheless count it as a true acrylonitrile-benzene product because the comparatively small yield from acrylonitrile alone would be reduced by a further three-quarters on eqimolar admixture with benzene.

The adduct II could alternately undergo concerted hydrogen shift to V, whose subsequent dehydrogenation to biphenyl, while symmetry-forbidden if concerted, in contrast with that of IV,[8] cannot be ruled out at 650°. The transformation II→V is also

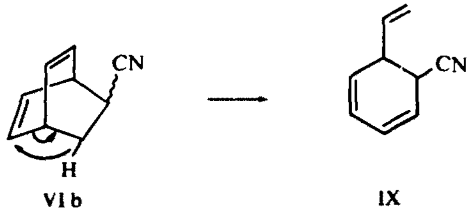
symmetry-forbidden, assuming the II results from all-cis addition,[7] but the alternative permitted shift to IV is sterically awkward.



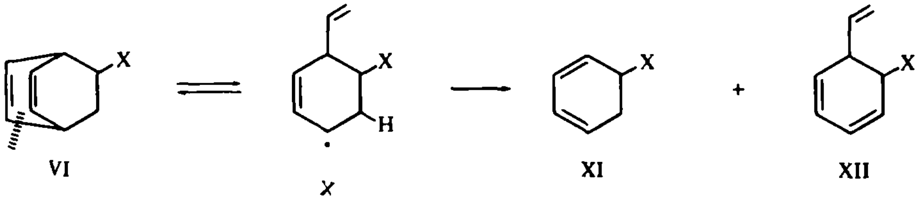
The formation of styrene from benzene and ethylene,[2] and of cinnamonitrile from benzene and acrylonitrile, can be explained by transformations of the primary adducts VI (X = H or CN) exactly analogous to those proposed above for the two different mechanisms on II.



In order to obtain *o*-cyanostyrene from VI by a concerted pathway, however, an initial hydrogen shift is required of a fundamentally different sort from those leading to V or VII. This step is symmetry-forbidden.



The diradical route, on the other hand, simply involves breaking one of the other allylic bonds in VI, leading to the diradical X, which affords both *o*-cyanostyrene and benzonitrile *via* XIb and XIIb, and styrene *via* XIIa.



Previously published interpretations of benzene's thermal reactions, particularly biphenyl formation, differ from ours. Suggested mechanisms include (1) primary fission of benzene to Ph· and H·,[9] (2) a four-center reaction forming biphenyl and H_2 from two benzene molecules,[10] and (3) formation of a donor-acceptor complex or phenylcyclohexadiene intermediate from two benzene molecules.[10] Mechanism (1) can be dismissed on simple grounds; formation of II involves a loss of *ca* 32 Kcal/mole in bond energy (loss: 2 C=C, 126,[11] and 2 benzene resonance energies, 72;[12] gain: 2 C—C, 166[11]), whereas the bond dissociation energy (BDE) of Ph-H is 112 Kcal/mole.[14] Mechanism (2) is symmetry-forbidden,[8] and furthermore does not explain the observation[10] that hydrogen exchange among benzene molecules is faster than biphenyl formation. The mechanism here proposed becomes identical with (3) if II is recognized as the intermediate, rather than phenylcyclohexadiene or the complex, and fits the hydrogen-exchange data perfectly if the early steps in the scheme are reversible, a reasonable supposition.

The proposed fission of VIb in the sense VI→X implies that II might also cleave in this way, affording *cis*-9,10-dihydronaphthalene XIII, and thence naphthalene (at 150–200°, XIII produces naphthalene only,[14] and at 350–400° 1,2- and 1,4-dihydronaphthalenes are obtained also;[15] the latter two substances form naphthalene at 650–658°). In accord with this expectation, naphthalene does accompany biphenyl in the pyrolysis of benzene.[16] The low naphthalene/biphenyl ratio (0·002) compared to the IX/cinnamonitrile ratio (*ca* 0·4) fits the diradical mechanism well. Thus, the minor modes of cleavage of II and VIb, leading to naphthalene and IX respectively, proceed *via* diradicals of similar resonance stabilities (cf Xb). However, the competing formation of biphenyl from II involves diradical III, which is better than its counterpart VIII arising from VIb, by the difference in stabilization energy between a cyclohexadienyl radical and an α-cyano radical. This difference may be gauged by comparing the BDE's of H—CH_2CN (86 Kcal/mole[3]) and H-Cyclohexadienyl (70 Kcal/mole[17]), but is probably smaller than 16 Kcal/mole because the α-cyano radical residue in VIIIb is more substituted than ·CH_2CN. A difference of only about 10 Kcal/mole is required to account for the 200-fold relative rate factor between IX and naphthalene.

Neither the reactions of benzene with acetylenes nor the pyrolysis of 1 are exceptional. The former are clearly diene-retrodiene syntheses, and the latter is easily rationalized as competitive sequences of cyclohexadiene-hexatriene valence isomerizations, 1,5-hydrogen transfers, and cyclobutane pyrolyses, all symmetry-allowed[8] for concerted transformations in this system.

In general, the retrodiene syntheses discussed above, and therefore (if the theory of microscopic reversibility is accepted) the Diels–Alder reactions as well, can easily be fitted to the diradical mechanism. Fully concerted mechanisms, on the other hand, involve at least some symmetry-forbidden steps, although for reactions at these high temperatures firm conclusions cannot be drawn.

EXPERIMENTAL

The apparatus consisted of a cylindrical quartz tube of diameter 1 in with appropriate ground-joint fittings above and below the heated zone. A thermocouple well ran the length of the tube down the center. The tube was coated 9 in of its length with High Temperature Instatherm, an electrically resistive metal, by the Ace Glass Co., Vineland, N.J. This gave exceptionally even heating, when the tube was well wrapped with asbestos tape and glass wool, for most of its length, with some fall-off in temp at both ends of the heated zone. The calculated reaction times do not take this fall-off into consideration. The heated portion was packed with catalytically inert alundum pellets, and had a net volume of 51 ml. In all experiments, after purging with N_2, heating to the desired temp, and shutting off the N_2 flow, samples were introduced by dropping directly on the alundum by means of a syringe pump supplied by the Harvard Apparatus Co., Cambridge, Mass. The effluent was condensed in an ice-cooled receiver. The results were not influenced by whether fresh or used alundum was employed.

Gas chromatography was performed on an Aerograph series 1700 machine, with either of two columns: 6 ft × ¼ in 3% QF-1 on 100/200 mesh Gas Chrom Q at 125°, and 10 ft × 14 in 20% Dow Corning 200 on 80/100 mesh Gas Chrom Z at 200° Injector temperatures were 200° or below, and helium flow always 60 ml/min.

Pyrolysis of benzene. Approximately 2·1 g benzene was introduced into the tube, heated to 656–659°, at 0·152 ml/min; the calculated residence time was 24 sec. The only important VPC peaks to 18. min on the QF-1 column were benzene and biphenyl (2·9 min). On evaporation, the effluent left 0·05 g solid which was biphenyl by IR; yield about 2·5%.

Benzene and cyanoacetylene. A mixture of 0·5 ml cyanoacetylene and 1 ml benzene was pumped at 0·198 ml/min into the tube at 662–665°; residence time 13 sec. The light brown effluent showed, in VPC on QF-1, important peaks only for volatiles (e.g., benzene), biphenyl and benzonitrile (1·4 min). Both substances were isolated from a concentrate by preparative VPC, and identified by IR and by mixed injection with authentic material, taking care to equalize the quantities of known and unknown.

Benzene and methyl propiolate. Benzene (3·9 g, 0·05 mole) and redistilled methyl propiolate (2·1 g, 0·025 mole) were reacted for 24 sec at 653–660° (0·152 ml/min). Rapid gas evolution was seen throughout at a bubbler situated at the exit of the ice-cooled receiver. The effluent was dark, with black particles. The VPC spectrum on QF-1 showed benzene, methyl benzoate, 1·4 min (1%), and many other substances. Repetition of the experiment at 0·297 ml/min (12 sec), and then at 0·583 ml/min (6 sec), effected no change in the height of the methyl benzoate peak while all others were steadily reduced except one other unidentified one at 1·2 min. A sample of methyl benzoate was isolated by preparative VPC and identified both by mixed injection and by its IR spectrum.

Benzene and acrylonitrile. A mixture of 15·6 g benzene (0·2 mole) and 10·6 g acrylonitrile (0·2 mole) was reacted at 660–668° using four flow rates (ml/min): 1·60, 0·816, 0·297 and 0·108. The calculated residence times were 2, 4, 11 and 30 sec respectively. The products from all four exhibited numerous VPC peaks, all with the same pattern, on both columns. In addition to unreacted starting materials, there were 5 major peaks, one of which was the expected biphenyl (10·5 min on DC-200). The effluent from the 30 sec run, 7·57 g, yielded 0·21 g oil after concentration (2·8%), from which the four unknowns were isolated by preparative VPC on DC-200, and identified as indicated. Benzonitrile, 2·8 min, by IR and VPC; *o*-cyanostyrene, 5·2 min, by NMR, IR and VPC comparison with a sample prepared by a known procedure;[19] *cis*-cinnamonitrile, 6·2 min, by IR and NMR; *trans*-cinnamonitrile, 7·4 min, by NMR and by IR comparison with an authentic sample.

Another set of 3 runs was made on an equimolar mixture of benzene and acrylonitrile, all at 0·212 ml/min, which corresponds to 15 sec reaction time at 650°. Temps were 596–604°, 546–550°, and 497–505°, and about 6 ml of the reagent mixture was used for each. After evaporation, the 600° run afforded *ca* 0·01 g oil (0·2%), the 550° run a trace only, and the 500° run, nothing. On QF-1, the 600° VPC spectrum resembled those from 650° reactions, but the proportions were different, with benzonitrile virtually eliminated. The 550° VPC pattern was markedly different from both, especially of course that from the 650° runs.

Pyrolysis of 7-cyano-4,2,0-bicylooctadiene-2,4 (I). One ml of I was introduced at 0·108 ml/min into the reactor at 652–672°. The calculated residence time would be 30 sec if cleavage to two molecules were rapid, and the first trace of effluent was visible 27 sec after commencement of addition. The effluent was mainly benzene and acrylonitrile by IR, and left 0·10 g on evaporation which was principally benzonitrile by IR and VPC on QF-1. The other small VPC peaks formed a pattern different from that normally exhibited by benzene and acrylonitrile at 650°.

Pyrolysis of trans-*cinnamonitrile.* Redistilled material (5·0 g) was passed into the tube at 0·15 ml/min at 653–664°; residence time 27 sec. The effluent, 4·6 g, was principally a mixture of *cis*- and *trans*-cinnamonitrile by VPC, with no *o*-cyanostyrene detectable. The peak corresponding to *trans*-cinnamonitrile was isolated by preparative VPC and had the correct IR spectrum.

Benzonitrile and acrylonitrile. A 4:1 (v:v) mixture of benzonitrile and acrylonitrile was reacted for 15 sec at 650–655°. The VPC spectrum was virtually identical before and after reaction, with no *o*-cyanostyrene detectable.

Pyrolysis of 1,2- *and* 1,4-*dihydronaphthalenes.* A 1:2 mixture of these compounds (1 part) and benzene (9 parts) was reacted for 16 sec at 650–658°. From 23 g effluent, 2·1 g semi-solid was obtained on evaporation which contained naphthalene by IR, and which was 40% naphthalene by VPC, with the remainder consisting chiefly of unreacted dihydronaphthalenes.

REFERENCES

[1] C. G. Krespan, B. C. McCusick and T. L. Cairns, *J. Am. Chem. Soc.* **83**, 3428 (1961); R. G. Miller and M. Stiles, *Ibid.* **85**, 1798 (1963); E. Ciganek, *Tetrahedron Letters*,3321 (1967); Cycloaddition of a benzyne to a pyridine ring has been reported; L. A. Walter, *J. Heterocycle Chem.* **6**, 979 (1969)

[2] M. Berthelot, *Liebigs Ann.* **142**, 251 (1867)

[3] J. A Kerr, *Chem. Rev.* **66**, 465 (1966); S. W. Benson, *J. Chem. Ed.*, **42**, 502 (1965)

[4] B. E. Job and J. D. Littlehailes, *J. Chem. Soc.* (C), 886 (1968)

[5] A. Wasserman, *Diels-Alder Reactions.* Elsevier, New York, 1965; R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.* **87**, 2046 (1965); J. Sauer, *Angew. Chem. Internat. Ed.*, **6**, 16 (1967); P. D. Bartlett, *Science* **159**, 833 (1968)

[6] E. R. Littman, *J. Am. Chem. Soc.* **58**, 1316 (1936); J. B. Harkness, G. B. Kistiakowsky and W. H. Mears, *J. Chem Phys.* **5**, 682 (1937); C. Walling and J. Peisach, *J. Am. Chem. Soc.* **80**, 5819 (1958); S. W. Benson, *J. Chem. Phys.* **46**, 4920 (1967)

[7] D. Bryce-Smith, *Chem. Comm.* 806 (1969)

[8] R. Hoffmann and R. B. Woodward, *Accts. Chem. Res.* **1**, 17 (1968)

[9] G. M. Badger, *Prog. Phys. Org. Chem.* **3**, 1 (1965)

[10] E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.* **88**, 21 (1966)

[11] T. L. Cottrell, *The Strengths of Chemical Bonds* (Second Edition) Butterworth's, London (1958)

[12] G. W. Wheland, *Resonance in Organic Chemistry.* Wiley, New York (1955)

[13] D. M. Golden and S. W. Benson, *Chem. Rev.* **69**, 125 (1969)

[14] E. E. van Tamelen and B. Pappas, *J. Am. Chem. Soc.* **85**, 3296 (1963)

[15] W. E. Doering and J. W. Rosenthal, *Ibid.*, **88**, 2078 (1966)

[16] E. K. Fields and S. Meyerson, *Chem. Commun.* 474 (1965)

[17] D. G. L. James and R. D. Suart. *Ibid.* 484 (1966)

[18] J. M. Stewart, I. Klurd and K. Peacock, *J. Org. Chem.* **25**, 913 (1960)